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Correlation of Metals with Hydrocarbons of Crude Oil in Maysan Province Southern Iraq

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Abstract: **It is known that Crude oil and its finished products contain mainly hydrocarbons, especially alkanes, naphthenic and aromatics. Hydrocarbons, which, composed mostly of carbon and hydrogen. Also, crude oil found to contain trace metal amounts of the element as well as oxygen and sulfur contained compounds. In order to clarify the relationship between hydrocarbons and trace metals in crude oil, separated samples of crude oil from four oil fields (Amarah field, Buzurgan field, Noor field, and Abogarab field) were collected and analyzed by Atomic Absorption spectrophotometer and Gas Chromatography to identify the trace metals, and hydrocarbons. The results revealed that the concentration of Mn ranged between (1385.1 to 1395.1) ppm, , Pb ranged between (62 to 87) ppm, Fe (14 to 30) ppm, Cu (6.9 to 29.1) ppm, Ni (17.1 to 27.3) ppm, Zn (10.6 to 21) ppm, Co (10.8 to 15.1) ppm, V (2.97 to 1.03) ppm, while the concentration of hydrocarbons from (C1 to C31) ranged from (0.02 to 3.46) wt% and other hydrocarbons (C32+) ranged (55.31 to 69.59) wt% in all field crude oil positions. In conclusion, there is a different amounts of trace metals found in crude oil, however, these metals shows a positive and negative correlation with oil hydrocarbons.**

Keywords: Trace Metals, hydrocarbons, compounds, Crude Oil, Concentration, Element. Petroleum, Aromatics, organometallic

I. INTRODUCTION

Crude oil and its finished products (Petroleum Products) contain mainly hydrocarbons, especially alkanes (paraffins), naphthenic, aromatics hydrocarbons, organometallic compounds and inorganic salts (metallic compounds). Hydrocarbons are mostly based on two elements carbon and hydrogen ranges from 84-87% carbon and (11-15%) hydrogen (ASTM D-4175). Fuel oil is a complex mixture of highly heterogeneous compounds of aliphatic (saturated), olefinic (unsaturated), aromatic and asphaltene hydrocarbons with significant amounts of additional elements, such as sulfur, oxygen, nitrogen and compounds containing metallic constituents, particularly; Vanadium, Nickel, Iron and Copper [1, 2, 3, 4]. Since petroleum is generated from organic matter of fine grained rocks, it is possible to correlate crude oils having a common source but reservoir in different horizons [5]. One of such ways of doing this is by analyzing the hydrocarbon fractions, Petroleum hydrocarbons fingerprinting (Gas chromatography fingerprinting) analysis for quantitative and qualitative oil characterization which is often used for evaluating the range of hydrocarbons in crude oil or rock extract [6]. The distribution of n-alkanes in crude oils can be used to indicate the organic matter source. Generally, short and medium chain, odd carbon numbered compounds of aliphatic hydrocarbons with carbon numbers between n-C15 and n- C25 are associated with aquatic sources, whereas shorter derivatives originate from lacustrine in contrast to mainly microphysics plants as sources of the longer chain derivatives [7]. The instrumental techniques of chromatography, ultraviolet and infrared spectroscopy together with mass spectrometry facilitate knowledge of the detailed hydrocarbon type composition of crude. The metal contents are present in crude oil either as inorganic salts, such as sodium and magnesium chlorides, or in the form of organometallic compounds, such as those of nickel and vanadium (as in porphyrins) [8, 9]. The total hydrocarbon composition and concentration of trace metals in crude oil varying from one paper to another, due to the place of study. Several studies investigated the presence of metals and hydrocarbons in crude oil to evaluating its petroleum system independent of the higher hydrocarbon makers in order to provide a quick and inexpensive way of understanding its petroleum system and result were different [5, 10, 11, 12, 13, 14, 15]. The aim of this study is to investigate the correlation of metals with a type of hydrocarbons in crude oil in Amarah city Maysan province Iraq.

II. MATERIALS AND METHODS

A. Sample Collection and Preparation

Four crude oil samples were collected from different fields, Noor field, Amarah field, Buzurgan field and Abogarab field in Maysan province south of Iraq. The determination of the metals in crude oil requires pretreatment to the sample before presentation to the instrument, hence our samples treated and digested in wet as seen in [16, 17].

B. Trace Metal Concentrations

Ten trace metal content in crude oil samples were measured by using Atomic Absorption Spectrometer (PgAA500) in Basra University Marine Science Centre.

C. Total Hydrocarbon Contents

Thirty two of the hydrocarbons content were measured by using Gas Chromatography Agilent (7890 A) in Maysan Oil Company Labs.

D. Correlation of Trace Metal and Hydrocarbons Content

The correlations between trace metal and hydrocarbons compounds in crude oil samples were done by using SPSS and EXCEL program.

III. RESULTS AND DISCUSSION

A. Trace Metals Concentration

The results showed that Mn the most abundant metal followed by Pb, Fe, Cu, Ni, Zn, Co, and V in Amarah field, While, Mn is the most abundant followed by Pb, Ni, Zn, Co, Fe, Cu, and V and in Buzurgan field. In addition Noor field and Abogarab field was the most abundant Mn followed by Cu, Pb, Zn, Ni, Fe, Co, and V and Mn followed by Pb, Ni, Fe, Co, Zn, Cu, and V respectively seen in table 1. These values are higher than the value which was reported by [18, 19, 20]. However the results of trace metal could be different due to the contact of crude oil with rocks contained this metal and the distribution of the metals is fairly homogenous in the samples. Also the difference in geological activity, and mineral accumulation during rock deposition. The relatively higher levels of Mn, Cu, Pb, Zn, Ni, Fe, Co, and V observed in the result except Cr, may explained by the fact that most soils associated with the areas of study are also associated with appreciable deposits of metal ores such as iron [20].

TABLE 1 CONCENTRATION OF THE TRACE METALS ASSOCIATED WITH CRUDE OIL IN DIFFERENT FIELDS (PPM)

Field Oil	**Mn**	**Cu**	**Pb**	**Zn**	**Ni**	**Fe**	**Co**	**V**	**Cr**
Amarah	1395.1	29.1	87	21	27.3	30	14.9	2.71	0
Buzurgan	1392.2	9.9	87	21	23	14	15.1	2.27	0
Noor	1386.5	125	74.8	61	28	26.2	14.1	2.78	0
Abogarab	1385.1	6.9	62	10.6	17.1	14.2	10.8	1.81	0

B. Hydrocarbons Content

The results of gas chromatography of crude oil samples showed in Table 3. Methane and butane were found to be the most abundant gases in these samples. The percentages of gases as well as the total percentage of the other alkane and alkene components were used as indicators to characterize the nature of the hydrocarbon mixture emitted by each sample [27.] The results also revealed that concentrations of (C1 to C31) hydrocarbons ranged from (0.02 to 3.46) wt% in all field of crude oil samples. From the summation of these results we obtained total petroleum hydrocarbon (TPH) that ranged from (30.44 to 44.97) wt% in Abogarab field followed by Buzurgan, Amarah, and Noor fields while the high concentration of hydrocarbons (C32+) ranged from (55.31 to 69.56) wt% in Abogarab field followed by Buzurgan, Amarah, and Noor fields. The highest concentrations were found of total petroleum hydrocarbons showings that terrestrial vascular plants contributed to n-alkanes in the study area and n-alkanes indicating an input of mixed marine and terrestrial organic matter [24].

TABLE 3 CONCENTRATIONS OF THE HYDROCARBONS ASSOCIATED WITH CRUDE OIL IN DIFFERENT FIELDS

Component	AMARAH Field Concentration WT%	Buzurgan Field Concentration WT%	NOOR Field Concentration WT%	ABOGARAB Field Concentration WT%
C1	0	0	0	0
C2	0.02	0.06	0.03	0.04
C3	0.15	0.2	0.12	0.12
*I-C4	0.11	0.2	0.13	0.1
**N-C4	0.44	0.5	0.37	0.28
I-C5	0.45	0.45	0.43	0.3
N-C5	0.74	0.67	0.57	0.4
C6	1.78	1.76	3.46	1.08
C7	2.46	2.25	2.02	1.49
C8	2.17	2.03	1.93	1.38
C9	2.23	2.06	2.05	1.38
C10	2.41	2.2	2.16	1.51
C11	2.07	1.97	1.94	1.35
C12	2.05	1.98	1.95	1.42
C13	1.95	1.89	1.87	1.4
C14	2.35	2.19	2.18	1.63
C15	2.36	2.2	2.21	1.65
C16	2.23	2.11	2.11	1.6
C17	2	1.89	1.88	1.42
C18	1.34	1.33	1.33	1.01
C19	1.9	1.8	1.8	1.35
C20	1.15	1.78	1.69	0.99

C21	1.36	1.14	1.16	1.03
C22	1.33	1.62	1.34	1.19
C23	1.45	1.34	1.44	1.04
C24	1.31	1.25	1.26	0.87
C25	1.3	1.25	1.28	0.78
C26	1.01	1.32	1.27	0.93
C27	1.22	1.13	1.23	0.74
C28	1.21	1.19	1.19	0.79
C29	1.12	1.09	1.19	0.77
C30	0.86	0.9	1	0.33
C31	0.16	0.34	0.38	0.07
Summation of C1 to C31	44.69	44.09	44.97	30.44
C32+	55.31	55.91	55.03	69.56
TOTAL	100%	**%100**	**%100**	**%100**

Note: sample density = 0.9744 g/cm^3 with 15.6 c
* I= ISO-
**N= NORMAL-

C. Correlation of Trace Metal and Hydrocarbons Content

Figures 1 and 2 shows the relationships between Mn, with hydrocarbons compounds in different field of crude oil. In this study Mn metals observed to increase in content with increasing of (C1 to C31) hydrocarbons while decrease with decreasing of (C32+) hydrocarbons. Figure 3 and 4 shows the metals Cu, Ni and Zn increase with the increasing of (C1 to C31) hydrocarbons while decrease with decreasing of (C32+) hydrocarbons. Figures 5 and 6 shows the metals Fe, Co, Pb, and V decrease with decreasing of (C1 to C31) hydrocarbons and increase in content with increasing of content (C32+) hydrocarbons increase. The difference of these results may be because metal as ion (+2) associated with hydrocarbons as porphyrins in crude oil. The porphyrin ring system is composed of four pyrrole rings joined by (=CH-) groups. Many metal ions can replace the pyrrole hydrogens and form chelates that have abundance of electrons to obtain orginometallic compound more regular chains and saturated. The chelate is planar around the metal ion and resonance results in four equivalent bonds from the nitrogen atoms to the metal to obtain hydrocarbons compounds. In addition, some metals have negative correlation with hydrocarbons (C32+) these hydrocarbons may not tend to form chelate sand more saturated and regularly, in addition due to different proportions of the various molecular types, sizes of hydrocarbons and other elemental constituents in the crude mix [21]

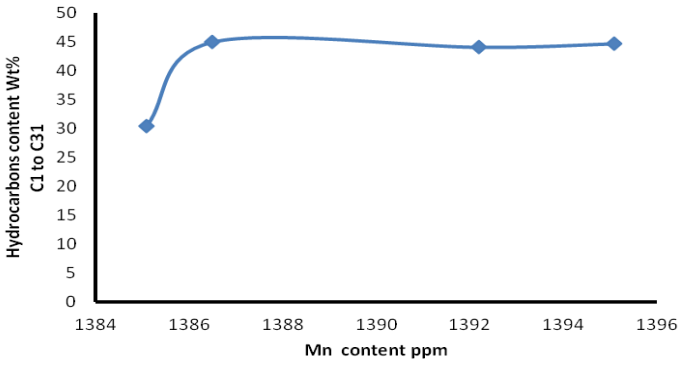

Fig 1 Correlation of Mn content with Hydrocarbons C1 to C31 in all fields

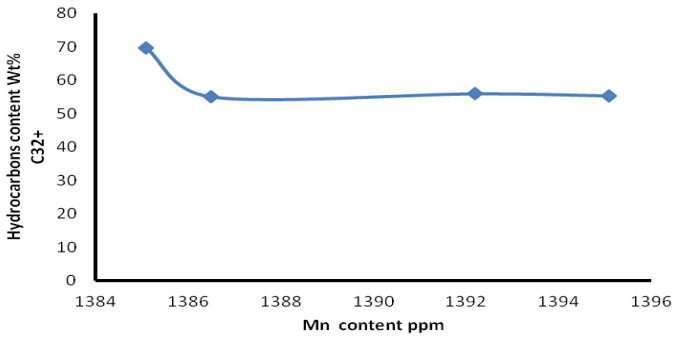

Fig 2 Correlation of Mn content with Hydrocarbons C32+ in all fields

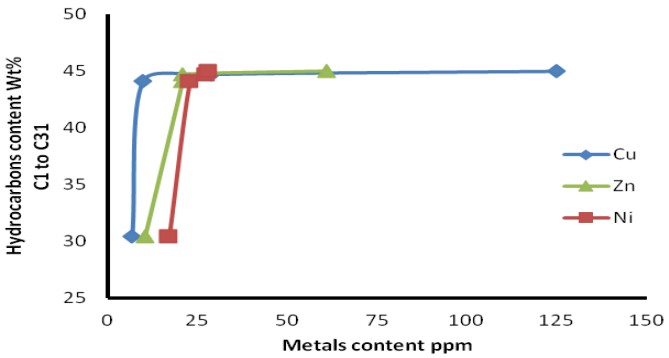

Fig 3 Correlation of metals content with Hydrocarbons C1 to C31 in all fields

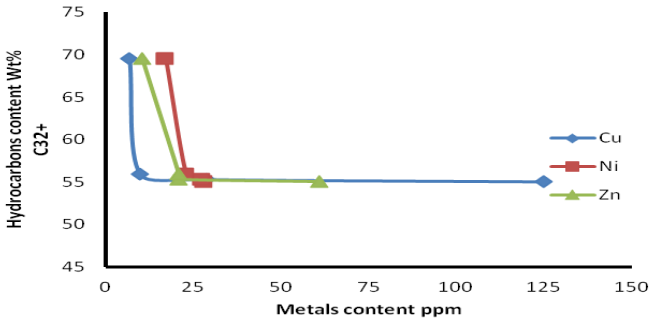

Fig 4 Correlation of Metals content with Hydrocarbons C32+ in all fields.

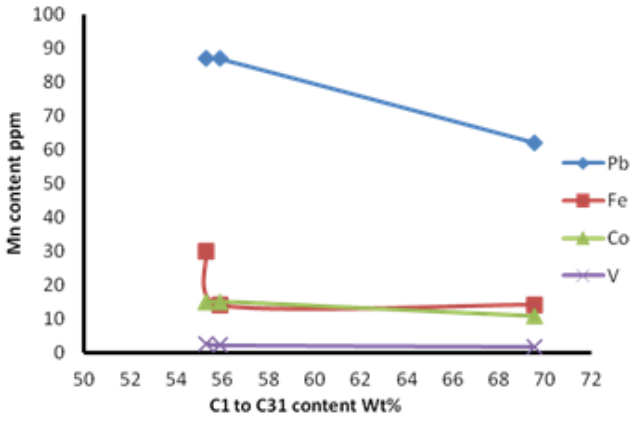

Fig 5 Correlation of metals content with Hydrocarbons C1 to C31 in all fields

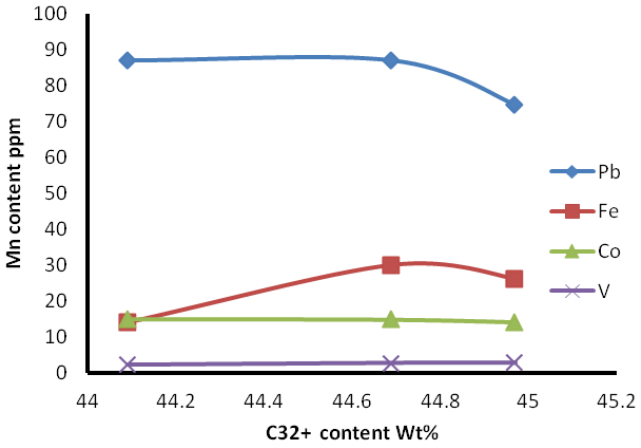

Fig 6 Correlation of Metals content with Hydrocarbons C32+ in all fields.

CONCLUSION

The current study determined a correlation between hydrocarbon content and metals such as correlation may result from. Also, this study found a different concentration of metals in crude oil samples that differ field to field, where showed higher concentrations of Mn followed by, Pb, Fe, Cu, Ni, Zn, Co, and V except Cr equal. The hydrocarbons content and organometallic compound were measured by using Gas Chromatography that shows the hydrocarbons from (C1 to C32+). Some of metal observed have correlations with hydrocarbons content, where increase with the increasing of (C1 to C31) hydrocarbons and decrease with decreasing of (C32+) hydrocarbons in samples of crude oil from four oil fields (Amarah field, Buzurgan field, Noor field, and Abogarab field) in Maysan province.

REFERENCES

[1] Oforka, N.C., Osuji, Leo C. and Onojake, M.C, Petroleum hydrocarbon fingerprinting of crude oils from umutu/bomu oil fields in Niger Delta, Nigeria, Archives of Applied Science Research, 2012, 4 (1):246-253.

[2] Onojake Mudiaga C. (Corresponding author), Trace Metals Geochemistry of Crude Oils from Umutu/Bomu Fields in South West Niger Delta Nigeria , Energy and Environment Research Vol. 1, No. 1; December 2011

[3] Nafi'u Tijjani, P.O Ike, B.B Usman, D. I. Malami and Alaere Matholo, Trace Elemental Analysis of Nigerian Petroleum Products Using AAS Method, International Journal of Scientific & Engineering Research, Volume 3, Issue 2, February -2012 .

[4] Sami Matar, Professor Lewis Hatch, Chemistry of Petrochemical Processes, 2nd Edition, 1994, 2000 by Gulf Publishing Company, Houston, Texas. All rights reserved. Printed in the United States of America, pp 19.

[5] Mark O. Onyema and Patience N. Manilla, Light Hydrocarbon Correlation of Niger Delta Crude Oils, Journal of American Science 2010, 6(6).

[6] Hunt, J.M., Petroleum Geochemistry and Geology. 1996. Freeman and company. New York, USA p. 231 – 238.

[7] Y. B. Mohammed1, H, Hamza2 and U. A. Danbatta, Application Of Organic And Inorganic Petroleum Geochemistry In Exploration And Exploitation Of A Prolific Basin: A General Review, Volume Journal of Environmental Science and Resources Management 4, December 2012.

[8] E.O. Odebunmi, E.A, Ogunsakin and P.E.P. Ilukhor, characterization of crude oils and petroleum products (I) Elution Liquid Chromatographic Separation And Gas Chromatographic Analysis Of Crude Oils And Petroleum Product, Bull. Chem. Soc. Ethiop.2002,16(2), 115-132.

[9] OSUJI, L C, ACHUGASIM, O, Trace Metals and Volatile Aromatic Hydrocarbon Content of Ukpeliede-I Oil Spillage Site, Niger Delta, Nigeria, J. Appl. Sci. Environ. Manage. June 2010, Vol. 14 (2) 17 – 20.

[10] A.K. Golovko, V.F. Kam'yanov, V.D. Ogorodnikov, The Physicochemical Characteristics And Hydrocarbon Composition Of Crude Oils Of The Timan–Pechora Petroliferous Basin, Russian Geology and Geophysics 53 (2012) 1216–1227.

[11] YE. B. FROLOV and M. B. SMm~OV, Higher Unsaturated Hydrocarbons In Crude Oils Higher Unsaturated Hydrocarbons In Crude Oils, Petrol. Chem. U.S.S.R. VoL 30, No. 1,pp: 34-45, 1990.

[12] Afnan Mahmood Freije, Heavy metal, trace element and petroleum hydrocarbon pollution in the Arabian Gulf: Review, Journal of the Association of Arab Universities for Basic and Applied Sciences (2015) 17, 90–100.

[13] Afrah A. Maktoof, Basim Y. ALKhafaji, Zahraa Z. Al-janabi, Evaluation of Total Hydrocarbons Levels and Traces Metals in Water and Sediment from Main Outfall Drain in Al-Nassiriya City/Southern Iraq, Natural Resources, 2014, 5, 795-803.

[14] G.O. Adewuyi1 & R A Olowu, Assessment Of Oil And Grease, Total Petroleum Hydrocarbons And Some Heavy Metals In Surface And Groundwater Within The Vicinity Of Nnpc Oil Depot In Apata, Ibadan Metropolis, Nigeria, IJRRAS 13 (1), October 2012.

[15] Nabil A.A. Al-Shwafi, Total Petroleum Hydrocarbon Carcinogens in Commercial Fish in the Red Sea and Gulf of Aden – Yemen, JKAU: Mar. Sci., Vol. 19, pp: 15-28 (2008 A.D. / 1429 A.H.).

[16] M.Y. Khuhawar, M. Aslam Mirza and T.M. Jahangir, Determination of Metal Ions in Crude Oils, Crude Oil Emulsions- Composition Stability and Characterization, ISBN 978-953-51-0220-5, March, 2012.

[17] Farooq Anwar, T.G.Kazi, Rubina Saleem, and M.I.Bhanger, Rapid Determination Of Some Trace Metals In Several Oils And Fats, Grasas y Aceites Vol. 55. Fasc. 2 (2004), 160-168.

[18] Mohammad F. All, Ahmed Bukharl, and Mohammad Saleem, Trace Metals in Crude Oils from Saudi Arabia, Ind. Eng. Chem. Prod. Res Dev. 1983, 22, 691-694.

[19] J. ELLRICH I, A. HIRNER and H. STRAK, Distribution Of Trace Elements In Crude Oils From Southern Germany, Chemical Geology, 48 (1985) 313--323 313 Elsevier Science Publishers B.V., Amsterdam --Printed in the Netherlands.

[20] Onojake Mudiaga C. Trace Metals Geochemistry of Crude Oils from Umutu Bomu Fields in South West Niger Delta Nigeria Energy and Environment Research Vol. 1, No. 1; December 2011.

[21] Onyema, Mark O. and Manilla, Patience N. (2010). Light Hydrocarbon Correlation of Niger Delta Crude Oils. Journal of American Science. 6(6):82-91.

[22] Thamer Khazal Al-Ameri, Ammar Ahmed Jaber Al-Tai, Study of Crude Oil types in the Mishrif Formation within Noor oil field Missan Governorate South Iraq.
[23] Peters, K.E., C.C. Walters, and J.M. Moldowan, The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments. 1999, Cambridge: Cambridge University Press.
[24] FAGBOTE, E. Olubunmi and OLANIPEKUN, Edward O, Characterization, Distribution, Sources and Origins of Aliphatic Hydrocarbons of the Soils of Agbabu Bitumen Deposit Area, Western Nigeria, African Journal of Scientific Research Vol. 10, No. 1 (2012).
[25] J. H. KARCHiiER AND E. L. GUNN, Determination of Trace Metals in Petroleum Fractions, Humble Oil & Rejining Co., Baytown, Tex. CHEMICAL SOCIETY, p. 4-0, 1951.
[26] Muhammad P.O. Ikeh B.B. Usman, B.G. Dan Shehu3 K. Salawu, D. A. Mikailu, Determination of Vanadium, Nickel, Copper and Iron as Complexes of Bis-Acetylpivalyl Methane (Ethylene Diamine) in Nigerian onshore and offshore Crude Oils Using HPLC, Journal of Natural Sciences Research, Vol.3, No.8, 2013.
[27] S. Goodman, The relationship between light hydrocarbons and carbonate petrology-a study from the Mendip Hills, Geological Journal, Vol. 22, 371-382 (Iy87